The Absolute Configuration of trans-Caronic and cis- and trans-Umbelluraric Acids

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Blätteralkohol (VIII) : Über das Vorkommen des *trans*-Isomeren in der natürlichen Blätteralkohol-fraktion

Akikazu HATANAKA und Minoru OHNO

Bull. Agr. Chem. Soc. Japan, **24**, 61 (1960)

Es wurde aufgeklärt, dass die in Tee-blättern weit verbreitet vorkommende natürliche Blätteralkohol-fraction aus einem Gemisch der *cis*, *trans*-Isomere besteht, wobei bisher das *cis*-Isomere stark überwiegt.

Darstellung von *n*-Hexin-1-olen und *n*-Hexen-1-olen

Akikazu HATANAKA, Masayuki HAMADA und Minoru OHNO

Bull. Agr. Chem. Soc. Japan, **24**, 115 (1960)

Die theoretisch möglichen sieben geometrischen Isomere von *n*-Hexen-1-olen und vier Stellungsisomere von *n*-Hexin-1-olen wurden in geometrisch reinen Formen erhalten. Die einigen davon waren zwar schon bekannt, aber in geometrischen Beziehungen sehen sie noch nicht ganz rein aus.

Vier Isomere von *n*-Hexin-1-olen, die Ausgangsmaterialien zur Darstellung der *trans*- oder *cis*-Hexen-1-olen wurden in jeden Fällen von Acetylen aus über Acetylennatrium in flüssigem Ammmoniak synthesitiert. Besonders war diese Darstellungsmethode von 4- und 5-Hexin-1-ol in der Ausbeute bedeutend überlegen als die bisherige. 2-, 3- und 4-*trans*-Hexen-1-ol und 5-Hexen-1-ol wurden durch die Halbhydrierung der entsprechenden *n*-Hexin-1-olen mit Natrium in flüssigem Ammoniak gewonnen, während 2-, 3- und 4-*cis*-Hexen-1-ol durch die Halbhydrierung in Gegenwart von Palladium-Bariumsulfat bei $-15°$ geliefert wurden. Diese Alkohole wurden über 3, 5-Dinitrobenzoat gereinigt. Die Infrarotspektren von diesen Verbindungen ergaben die verschiedenen interessanten Probleme.

The Absolute Configuration of *trans*-Caronic and *cis*- and *trans*-Umbelluraric Acids

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J. Amer. Chem. Soc., **82**, 5255 (1961)

Partial asymmetric syntheses of (−)-, and (+)-*trans*-caronic acids were achieved by addition of ethyl diazoacetate to (−)-menthyl senecioate and by that of dimethyldiazomethane to (−)-dimenthyl fumarate respectively in 15.9% and 6.3% optical yields. These results provide cogent support for the use of Prelog-Cram model to this asymmetric synthesis. The addition of ethyl diazoacetate to (−)-menthyl α-isopropylacrylate gave (−)-*cis*-, and (−)-*trans*-Umbellularic acids. Bas-

ed on asymmetric synthesis, (1R : 2R) and (1R : 2S)-configurations were assigned to these isomeric acids and consequently the absolute configuration of (−)-*cis*-umbellularic acid revealed all the configurations of terpenoids of thujane series.

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A Study of the Absorption Spectra of Cerium in Glasses

Megumi TASHIRO, Naohiro SOGA and Sumio SAKKA

Yogyo Kyokaishi (Journal of the Ceramic Association, Japan), **68**, 132 (1960)

The absorption bands of cerium in trivalent and tetravalent states in silicate and phosphate glasses, whose exact positions are still open to discussion, and the effects introduced by the change of composition and of melting condition were investigated.

For the measurement of the absorption spectra of silicate glasses with poor ultraviolet transmission the thickness of the sample plates was reduced to 0.12～0.02mm by polishing.

The results obtained are as follows: (1) In the silicate glass consisting of K_2O, BaO, and SiO_2, Ce^{3+} gives a sharp and weak absorption band at 320 mμ, whereas Ce^{4+} gives a broad and strong absorption band in ultraviolet region below 350 mμ. (2) In the phosphate glass consisting of K_2O, BaO, Al_2O_3 and P_2O_5, Ce^{3+} gives three sharp and weak absorption bands at 294, 245, and 227 mμ, whereas Ce^{4+} gives a broad and strong absorption band in ultraviolet region, as before.

Studies on the Mechanical Strength of the Photosensitive Opal Glass

Megumi TASHIRO and Sumio SAKKA

Yogyo Kyokaishi (Journal of the Ceramic Association, Japan), **68**, 158 (1960)

When a lithium containing photosensitive glass is exposed to ultraviolet light and then subjected to the heat treatment, it changes into a polycrystalline material characterized by its good mechanical properties (S.D. Stookey, *Ind. Eng. Chem.*, **45**, 115 (1953)).

The purpose of this paper is to present the relation between the mechanical strength and the grain size of the constituent crystallites of the resultant material.

Glass specimens (2.5×5×5 0mm) of the oxide composition SiO_2 81, Li_2O 12.5, K_2O 2.5, Al_2O_3 4, CeO_2 0.03, Au 0.027% (wt.) were exposed to ultraviolet light by placing them at a distance of 10 cm from a 500 watt high pressure mercury lamp for 2 to 1000 min. After the exposure they were heated at three steps; first at 510°C for 30 min. to cause formation of gold nuclei, then at 620°C for 60 min. to